

Influence of Fires on Air Quality During the SEAC⁴RS 2013 Campaign

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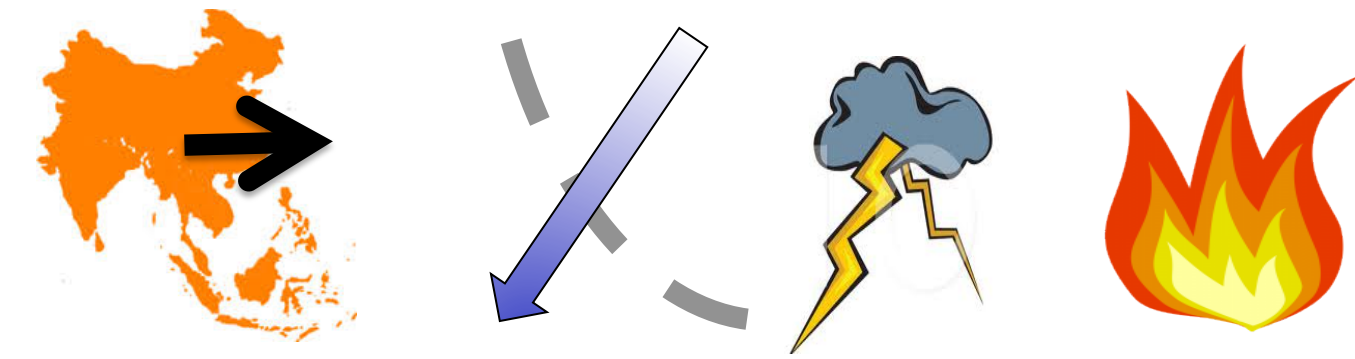
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1. Motivation

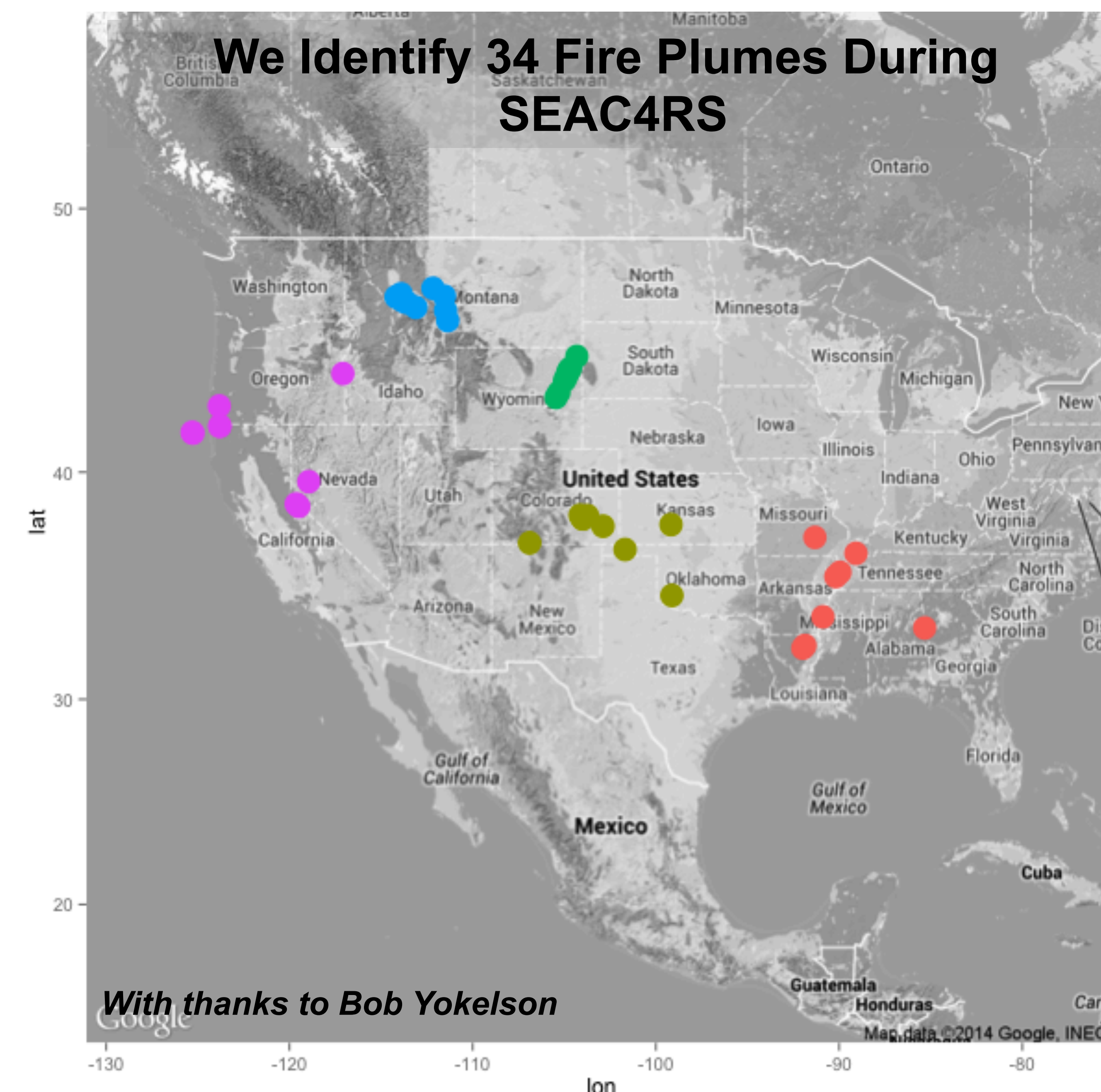
Ground-level O₃ pollution is a serious public health and environmental concern in the U.S. I am interested in improving understanding of background O₃, a critical issue for setting the National Ambient Air Quality Standards (NAAQS). EPA is considering tightening the O₃ NAAQS, but it is **unclear to what extent uncontrollable background O₃ would hinder achievement of a lower NAAQS (Macdonald-Buller et al, 2011).**

Addressing this issue is of critical importance for policy and presents a major scientific challenge to coupling atmospheric chemistry on global and regional scales.

Background O₃ is not directly measurable and thus must be calculated from a global chemical transport models (CTM). Current CTMs have difficulty capturing observed high background ozone events (over 70ppb) due a variety of limitations including modeling of wildfires¹. CTMs also show large differences in their representation of the impact of wildfires on the ozone background (Fiore et al, 2009) which is very problematic for air quality policy.



2. Fires Sampled During SEAC⁴RS



Plumes with high $\Delta O_3/\Delta CO$ have enhanced PAN. PAN may be an important NO_x reservoir for downwind O₃ production as well. Thus successful modeling of fire impacts on background ozone requires successful modeling of PAN.

Mean $\Delta O_3/\Delta CO$ – ppbv/ppbv

km	SE (n=5)	Central (n=8)	Wyoming (n=5)	NW (n=9)	California (n=7)
0-1	0.0	-	-	-	-
1-2	0.0	-	-	-	0.02
2-3	-	0.08	-	-	0.02
3-4	0.04	0.09	-0.02	-0.02	0.02
4-5	0.15	0.07	0.13	0.01	0.07
5-6	-	0.05	-0.01	-	-

Mean $\Delta PAN/\Delta CO$ – pptv/ppbv

km	SE (n=5)	Central (n=8)	Wyoming (n=5)	NW (n=9)	California (n=7)
0-1	-0.7	-	-	-	-
1-2	-0.9	-	-	-	2.6
2-3	-	7.8	-	-	3.9
3-4	5.5	9.1	3.6	4.6	4.1
4-5	6.8	5.0	9.1	4.4	4.5
5-6	-	5.6	6.3	-	-

3. Geos-Chem NO_x-O₃-VOC Simulation

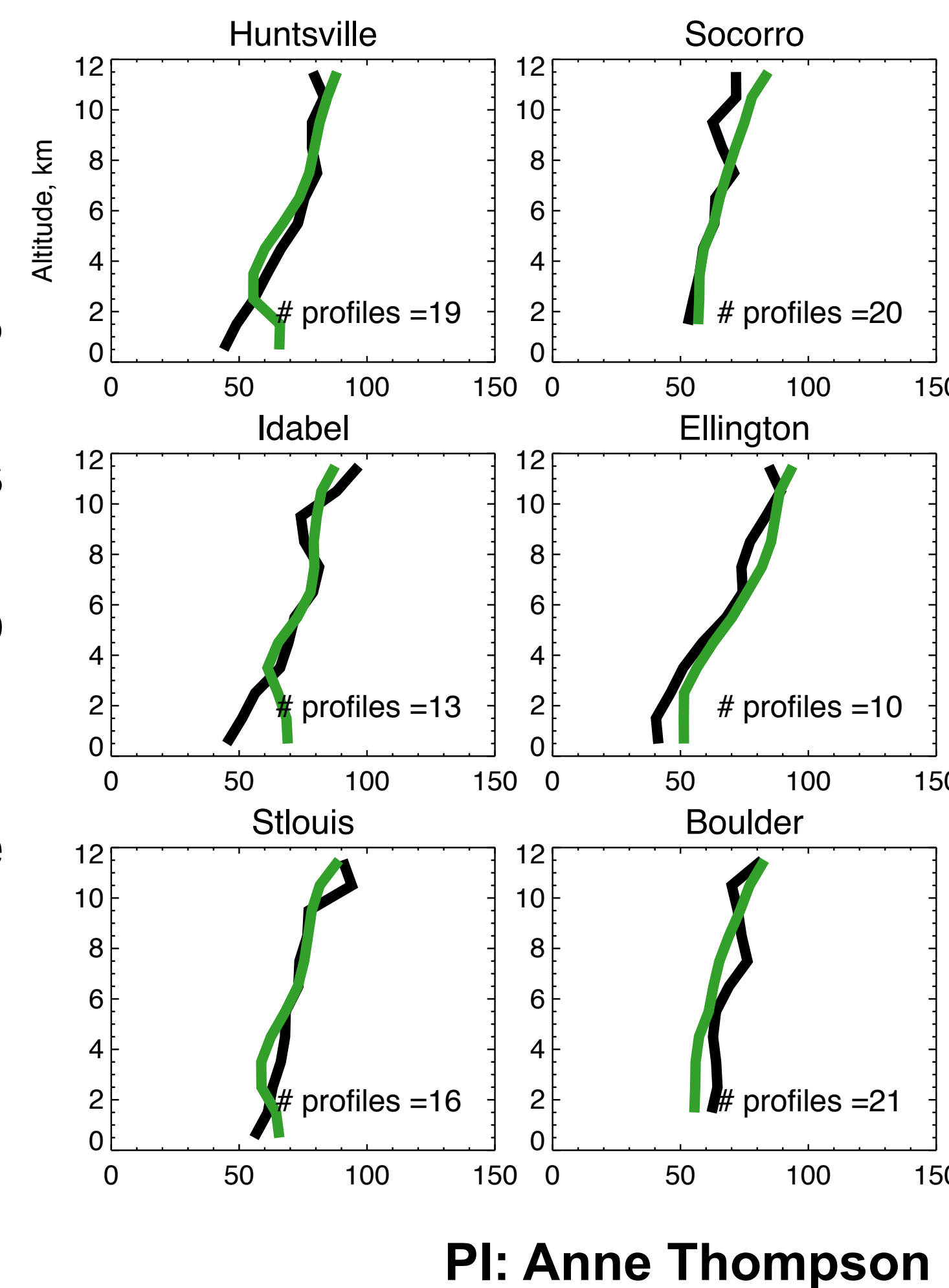
- Resolution = 0.25° x 0.3125° and 4°x5°
- Meteorology = GMAO GEOS-FP
- Emissions = NEI2008, FINN, MEGAN2.1
- Soil NO_x = Hudman et al, 2012
- Isoprene chemistry = Mao et al, 2013

Fire Injection

- Emit 40% of NO_x as PAN and 20% as HNO₃ (Alvarado et al, 2010).
- Inject 15% into 3-5km in the West to match SEAC⁴RS observations.
- For the rest of the northern midlatitudes, inject 15% into the first few km of the free troposphere.

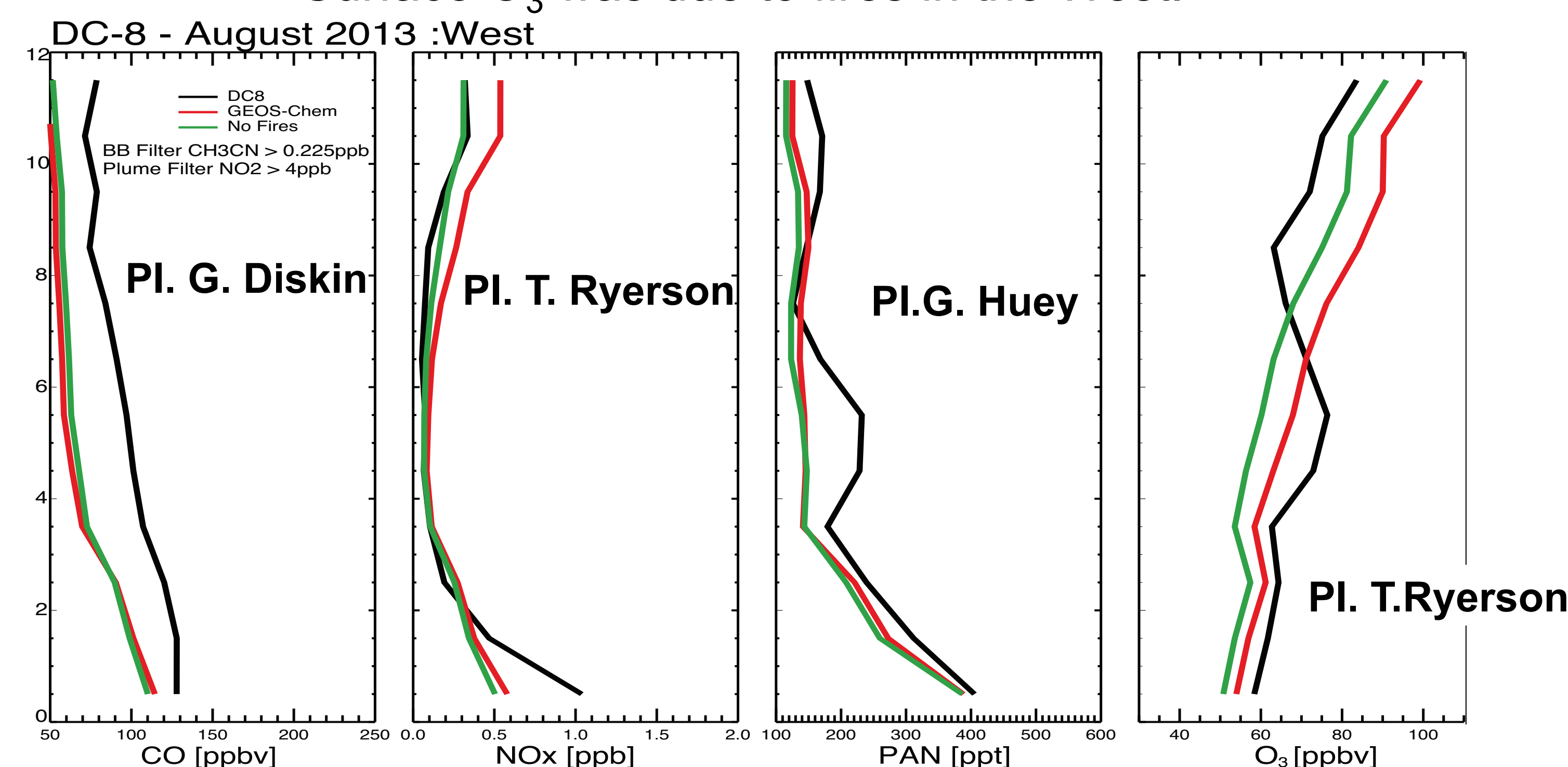


Geos-Chem O₃ compares well with SEACIONS in the free troposphere.



4. Modeled Impact of Fires on Surface O₃

Geos-Chem Predicts that During the SEAC⁴RS Time Period, ~4ppb of Surface O₃ was due to fires in the West.



Geos-Chem overall underestimate surface ozone in the West which may be due to inadequate VOC and NO_x emissions from either fires or anthropogenic sources.

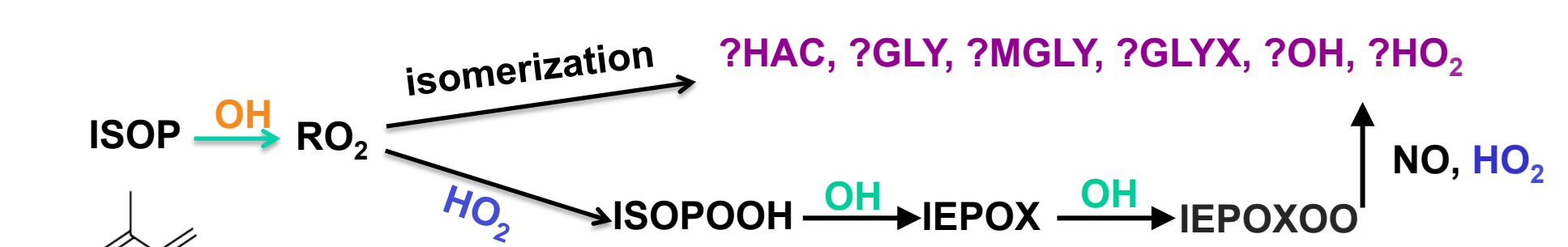
5. Future Work

Free Tropospheric O₃ in the West:

- Improve modeling of near-source VOC chemistry from fires, and resultant ozone and PAN formation, in collaboration with Matt Alvarado using the ASP model.

Southeast U.S. Chemistry:

- Proper treatment of new isoprene oxidation products:
 - Wet and dry deposition
 - Aerosol uptake
 - Transport
- Incorporate the most recent studies on epoxides and isomerization to test uncertainties in these mechanisms.



6. Conclusions

O₃ chemistry in the southeast U.S. is sensitive to the products from isomerization and epoxides. The general problem of CTMs in overestimating O₃ in the southeast and underestimating O₃ in the West persists.

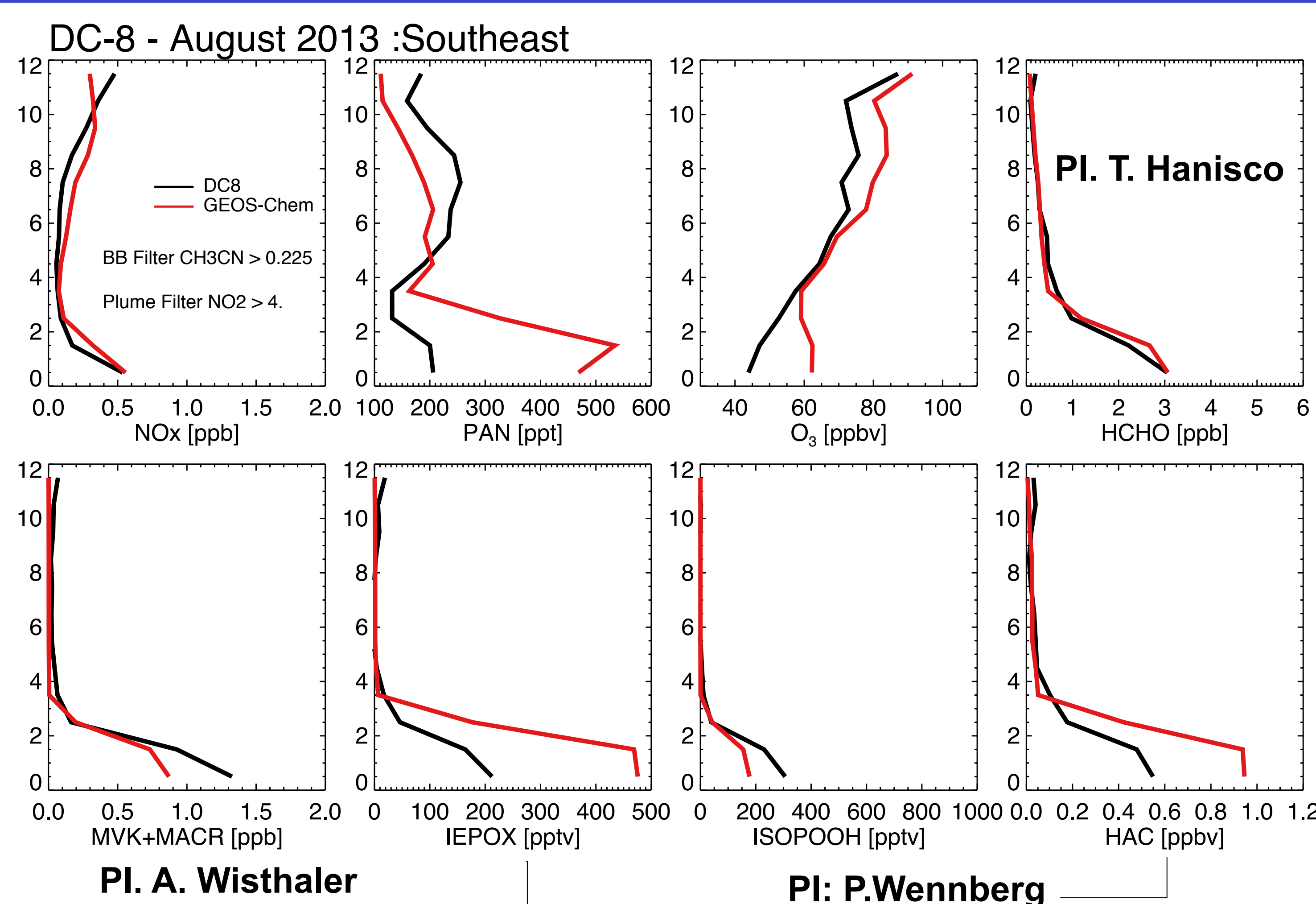
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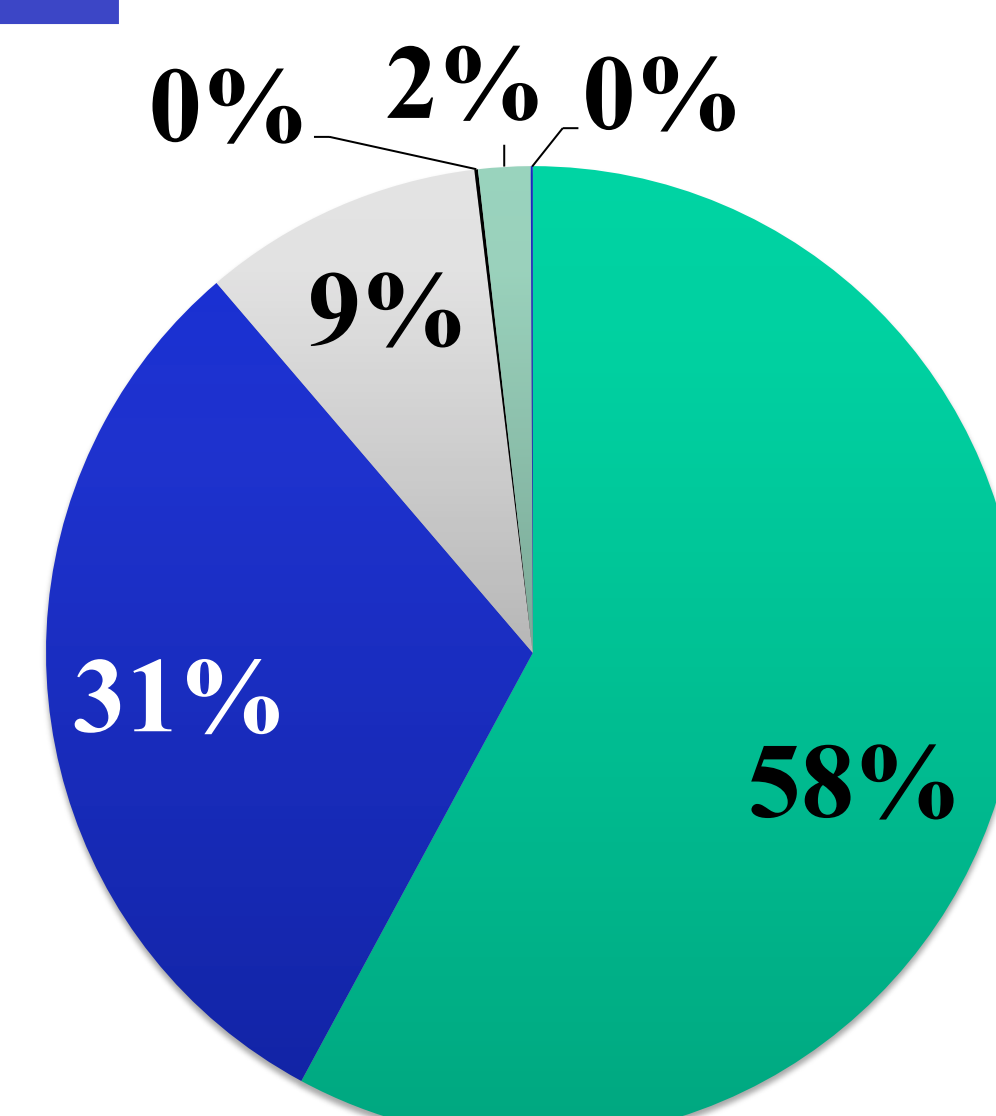
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4. Modeled Southeast U.S. Chemistry

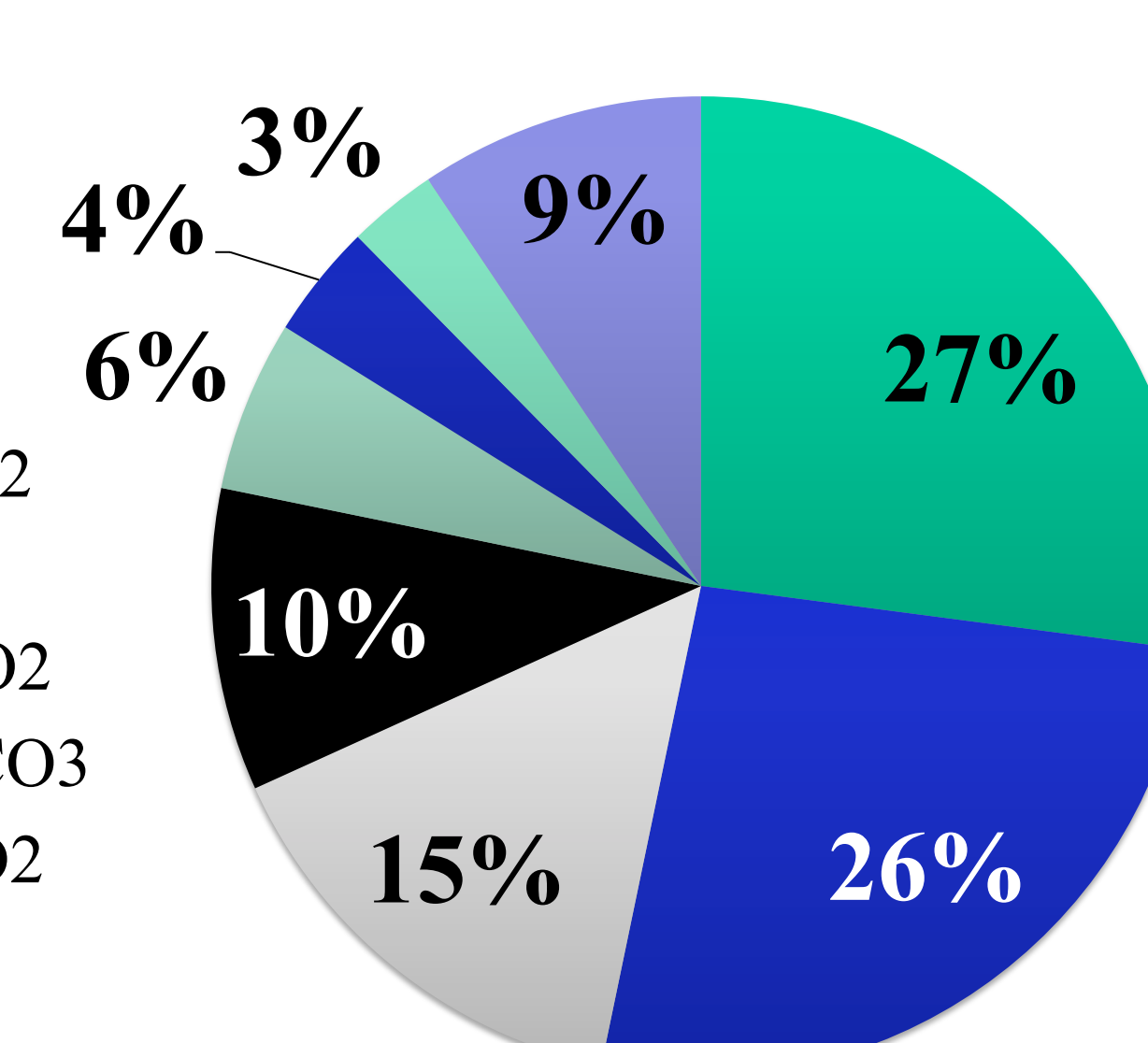


Fate of Isoprene Hydroperoxy Radical (RIO2) - Southeast



- RIO2 + NO
- RIO2 + HO2
- RIO2 Isom
- RIO2 + RIO2
- RIO2 + MCO3
- RIO2 + MO2

Peroxyacetyl Radical Generation: Southeast



- MGLY (hv)
- ALD2 + OH
- MGLY + OH
- VRO2 + NO
- VRO2 + HO2
- MAO3 + NO
- ISOP + O3
- Other

The isomerization pathway compares well with the findings of Crounse et al, 2011. However, in the southeast, MGLY from photolysis and OH oxidation accounts for ~50% of the PA radical. MGLY comes from HAC oxidation, various parts of MVK oxidation, and directly from isoprene RO₂ oxidation. Approximately 50% of the HAC comes from isomerization as well, with 25% coming from epoxides. Therefore it is difficult to reconcile measured PAN and O₃ with the isomerization schemes currently available (Peeters et al, 2009, Crounse et al, 2011, Fuchs et al, 2013) with the epoxide chemistry adding additional uncertainty (Jacobs et al, 2013, Bates et al, 2014).